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IMPARTING ANTIMICROBIAL PROPERTIES TO FIBERS

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Imparting Antimicrobial Properties to Fibers

by

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IMPARTING ANTIMICROBIAL PROPERTIES TO FIBERS

Imparting to fibers antimicrobial properties (antimicrobial, antifungal, antiprotozoal, and, possibly antiviral chemotherapeutic activity) has two basic aims: (1) protecting the fibers against the action of microorganisms, and (2) protecting objects which come in contact with fibers against the action of pathogenic microflora.

Antimicrobial fibers and fabrics thereof directly for medical purposes can be utilized as bandage and suture material in surgery, as antiseptic masks in operations, as underwear and bedlinen and clothing, for prophylaxis in fungal diseases (as stockings, gloves, headgear, etc.), for the production of prostheses in cardiac-vascular and other surgery, and possibly also for the treatment of diseases of a protozoal nature.

The technical use of antimicrobial fibers includes the utilization of fabrics thereof in the form of filters for decontaminating water and air in buildings, the production of fishing accessories stable against the action of different microorganisms, technical fabrics not subject to rotting, antiseptic packaging material, etc.

Besides the indicated special fields of application, antimicrobial fibers are also of general consumer importance. They possess better hygienic properties than ordinary fibers, they decrease the possibility of acquiring infectious diseases, they are subjected to rotting with greater difficulty, and, finally, they can hinder the development of an unpleasant odor due to insufficiently clean clothing.

Imparting antimicrobial activity to fibers can be carried out in two ways:

- 1) by sorption of chemotherapeutic preparations or antiseptic agents (with subsequent desorption) and

- 2) by chemical linking of the fiber with compounds which impart to the fibers an antibacterial effect (with their subsequent cleavage).

The fixation of antimicrobial agents by sorption is, in its turn, achieved by two methods.

The first of these consists in subjecting the fibers of fabrics to impregnation with the proper agents. For this purpose, use is usually made of quarternary ammonium compounds, halogen-containing salicylanilides, trichlorcabanilide, neomycin, organomercury preparations, hexachlorine, and other phenol compounds [1]. A disadvantage of this method is that the applied reagents do not possess sufficiently firm linkage with the fiber and are easily removed during washing. Articles of such fibers should in the course of their use be periodically impregnated with the proper agents, which is, of course, not economical and not convenient in use.

In accordance with the second method, the sorption linkage between the fiber and antibacterial preparation is accomplished by the introduction of biologically active agents into the spinning solutions (or melds) from which the fibers are subsequently spun. In this method, the substance is uniformly dispersed to the entire mass of the polymer and enters into the fine structure of fiber, which takes shape during the spinning process. As a result of this, the washout of the preparations from the fibers during use is made difficult, which facilitates an increase in the service life of the articles.

In our laboratory, by introducing preparations of nitrophenylacetate, phenylhydrazine, as well as iodine, into the spinning solution that was synthesized in the Institute of Organic Syntheses, Academy of Sciences USSR the wet method of spinning yielded antimicrobial polyvinyl alcohol and polyacrylonitril fibers.

The introduction of antibacterial preparations into the spinning mass involves practically no difficulty even when the polymer is in solution. This operation is complicated when the fibers are spun from the meld. As is known, such widely used fibers as polyamids and polyesters are spun from melds. In this instance, two types of difficulties develop. The first of these is related with the difficulty of mixing the substances and highly viscous systems which the polymer melds are. For this reason, it is expedient to apply the antimicrobial preparations on the resin crumbs even before it is molten and, in such a way as is done in the production of dull fibers. The second difficulty stems from the fact that through the spinning of the fibers from the meld, the polymer is heated to a temperature in the order of 250° C and higher. Consequently, it was necessary to employ preparations which have a high decomposition point, for otherwise, they lose their activity even at the very start of the fibers spinning. By using this method, we were able to introduce into the polyamide fiber the above indicated phenylhydrazine preparation. In a similar manner, the Japanese firm Toray and others have recently produced a bactericidal nylon fiber and intend to mass produce polyester and polypropylene fibers with the same properties, by using a preparation having the code name of "permakem" [2].

In order to impart antimicrobial properties into natural fibers, only the method in which the preparations are applied on the fiber by impregnation is suitable. Of course, this does not pertain to the possibilities that have been opened by reactions of polymer analogue conversions which are accompanied by fixation to the fiber of chemotherapeutic substances or preparations - antiseptics by means of a chemical bond.

In this case, the fiber and the antibacterial substance represent one polymer compound. The chemical nature of the bond between the fiber and the reagent insures the most prolonged action which is preserved practically in the course of the entire use period of the articles.

The problem of the fixation of antimicrobial substances on the fiber by means of a chemical bond contains, at first sight, two contradictory postulates. Actually, on the one hand it is dictated by the effort to prevent the removal of groupings which are responsible for the antimicrobial effect from the fiber during the use and on the other hand - it is necessary to assure the transportation (diffusion) of these groups within the microbial cells for otherwise, the main goal of destroying the pathogenic microflora at a distance will not be achieved. The solution of this contradiction is as follows: the chemical bonds, even such as the firm covalent bond can be weakened to a certain degree and, under definite conditions, the antimicrobial substance which is linked with the fiber is cleaved from it, true, in extremely small doses. Quantitatively, this substance is so small that its cleavage does not in any way effect the properties of the fiber, including also the antibacterial activity of the latter. Nevertheless, it can be rather sufficient to effect microorganisms. From this it is clear that the greatest activity will be possessed by fibers which are linked with the more strongly acting antimicrobial preparations, although much depends also on the nature of the chemical bond of the preparation of the fiber.

This principle was for the first time formulated and used by us in order to develop polyvinyl alcohol fibers with antibacterial action [3]. The activity of antimicrobial cellulose fiber developed by Z. A. Rogovin [4] has been based on this same principle.

There is no doubt that in such a way it is possible to impart antimicrobial properties also to other (probably to all) fibers whether they are chemical or natural. Besides, in the case of regenerated and synthetic fibers, the accomplishment of a chemical bond with disinfecting substances can be achieved not only after the spinning of the fibers, but also during the preparation of the polymers for spinning and even earlier - during the polymerization stage.

Antibacterial substances can be fixed in the fiber through chemical bonds of three types: coordination, ionic, and covalent, the most firm of these is the covalent bond.

An example of the accomplishment of the coordination bond is the iodine-polyvinyl alcohol fibers which have been prepared by us [3]. These possess a very high antibacterial activity even with respect to the spore cultures (anthracoid). These fibers can be produced as water soluble as well as water insoluble. The activity drops a considerable degree after washing in hot water and at high temperatures. Nevertheless, during use under ordinary conditions they preserve their activity in the course of a long period of time. Thus, the activity of fibers checked one year after production was practically unchanged. These fibers represent a complex compound of iodine with polyvinyl alcohol, in which the iodine, in the opinion of a number of researchers, is in the form of cation [5].

The addition of antimicrobial substances to fiber by means of an ionic bond [6] is accomplished through ionogenic groups which are first introduced or created in fiber. If the cations or anions of these groups (depending on the nature of the resulting ion-exchange agent), are exchanged then for cations or anions of chemotherapeutic preparations or antiseptics, then the fiber acquires antimicrobial properties. This effect in this case will be determined by the ionization of the corresponding functional groups, as a result of which the dissociated ions of the antibacterial substances will exert on the substrate an action that is specific of these. In accordance with this method, we introduced into polyvinyl alcohol fiber silver, copper, mercury, arsenious acid, phenolic and salicylate preparations. Particularly effective were fibers which contained silver ions. Although the antimicrobial action of mercury-containing fibers is expressed more strongly, nevertheless, the utilization is limited because of the high toxicity of mercury ions.

Such preparations as nitrophenylacetate, NPP, and certain others were fixed on polyvinyl alcohol fibers by means of a covalent bond [7]. The fibers in this case acquire a high antibacterial (staphylococci, intestinal bacillus), antifungal (candida, trichophyton, epidermophyton), and anti-protozoal (trichomonas) activity. Inasmuch as it was observed above, the covalent bond possesses the greatest strength, in order to insure constant diffusion of the antimicrobial substances in the fiber, it is necessary to weaken the article. This is achieved by heating the fiber in a moist state or by wetting (washing) in detergents of an acid nature or simply or weakly acetic aqueous solutions.

An interesting trend in the development of antimicrobial fibers can be the dyeing of ordinary fibers with dyes that contain groupings which determine the antimicrobial and other activity. The utilization of combined properties of the dye and the antimicrobial preparation in one substance is promising also in a technical-economic respect. Chemical fibers can be subjected to such type of dyeing, but the processing can be carried out also in bulk or even during the stage of the polymer preparation.

In all cases of the use of fibers with an antimicrobial activity, regardless of whether it has been achieved through sorption of the proper substances or by accomplishing a chemical bond with these, the necessary

conditions for the manifestation of antibacterial action is the presence of moisture. It is precisely this which accomplishes the transport of active ingredients of fiber to the microorganisms. For this reason, and the liquid medium, the antimicrobial fibers act with greater effect. Nevertheless, in the presence of sufficiently active antiseptics or chemotherapeutic preparations, the possibility is not excluded of the inhibition of the microorganisms by the fibers also in dry media (in the air) since in this case the fibers themselves as well as the surrounding air contain a definite amount of conditioned moisture. The action mechanism of the antimicrobial fibers by means of the moisture of the medium can be considered as established.

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13. ABSTRACT

A brief review is given of existing methods for imparting anti-microbial properties to fibers and fabrics. The salient features of the methods, their advantages and disadvantages, and the properties of the resulting antimicrobial fibers are described.

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